

FORM P1

REPUBLIC OF SOUTH AFRICA  
PATENTS ACT, 1978APPLICATION FOR A PATENT AND ACKNOWLEDGEMENT OF RECEIPT  
(Section 30(1) - Regulation 30)

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1685

The grant of a Patent is hereby requested by the undermentioned applicant(s) on the present application filed in duplicate

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54	Title of invention
	PROCEDE DE SYNTHESE DE PERFLUOROSULFONAMIDES, DE PERFLUOROSULFONIMIDES ET DE LEURS SELS, AINSI QU'UN REACTIF DE SULFONYLATION

<input checked="" type="checkbox"/>	The applicant claims priority as set out in the accompanying form P2. The earliest priority claimed is FR 97/08084 18 May 1997
<input type="checkbox"/>	This application is for a Patent of Addition to Patent Application No.
<input type="checkbox"/>	This application is a fresh application in terms of S 37 and based on Application No.
<input type="checkbox"/>	This application is accompanied by:
<input checked="" type="checkbox"/>	1a A single copy of a provisional specification of pages
<input type="checkbox"/>	1b Two copies of a complete specification (in the French language) of 16 pages
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<input type="checkbox"/>	2b Formal drawings of sheets
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<input type="checkbox"/>	13a Request for delay of acceptance on form P4
<input type="checkbox"/>	13b

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Date 18 May 1998

For the Applicant

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18 MAY 1998

PATENT VAN BATEMENTE, MODELLE,  
BESLUITEN EN OUTEURSREG

FORM P7

REPUBLIC OF SOUTH AFRICA  
PATENTS ACT, 1978

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**COMPLETE SPECIFICATION**

(Section 30(1) - Regulation 28)

21	01	Official Application No	22	Lodging Date	47	J & K Reference
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51	International Classification					
	C07C					
71	Full name(s) of applicant(s)					
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72	Full name(s) of inventor(s)					
	PEVERE, Virginie; MARX, Emmanuel					
54	Title of invention					
	PROCESS FOR THE SYNTHESIS OF PERFLUOROSULPHONAMIDES, OF PERFLUOROSULPHONIMIDES AND OF THEIR SALTS, AND OF A SULPHONYLATION REAGENT					

PROCESS FOR THE SYNTHESIS OF PERFLUOROSULPHONAMIDES, OF  
PERFLUOROSULPHONIMIDES AND OF THEIR SALTS, AND OF A  
SULPHONYLATION REAGENT

5           The subject-matter of the present invention is  
a process for the synthesis of perfluorosulphonamides  
and of perfluorosulphonimides. The latter can be  
obtained in the form of their salts. The present inven-  
tion is also targeted at a perfluorosulphonylation  
10 reagent.

It more particularly relates to a reaction for  
the sulphonylation of a nitrogenous functional group  
carrying an electron-withdrawing radical. It is also  
particularly targeted at the sulphonation of a  
15 sulphonamide, in particular a fluorinated sulphonamide.  
The synthesis of sulphamides is in particular targeted  
at the case where the sulphamide is prepared with the  
aim of a subsequent sulphonation (in a second stage, in  
the same reactor, or simultaneously in situ).

20           Fluorinated sulphonimide derivatives are  
increasingly being developed for electrical applica-  
tions and in particular for forming batteries and for  
their catalytic power. The most frequently used  
compound derived from these sulphonimides is the  
25 lithium derivative, that is to say the salt of this  
imide, an imide which is itself very acidic.

The synthesis of these sulphonimides has  
already been carried out but employs processes which  
are particularly problematic and difficult to use.

30           The inserted Application WO 97/23.448 describes  
a process which, like all those which have preceded it  
(cf. FR-A-2,724,380), uses perfluoroalkanesulphonyl  
fluorides, the reactivity of which is very specific and  
the by-product of which is the fluoride ion, which  
35 requires the use of equipment which is resistant  
thereto and thus expensive, as well as exhaustive  
removal before discharge of the effluents. The very  
high volatility and the operating conditions result, in  
the commonest cases, in the operation being carried out  
40 under relatively high pressures. To cap it all, the

sensitivity to water of perfluoroalkanesulphonyl fluorides seems, in the light of this document, particularly high.

A few trials have been carried out on sulphonyl halides but have resulted in failures (for the problems relating to these syntheses, see Application WO 90/11.999, in particular page two, lines 30 to 35 et passim). This is in particular the case with bistrifluoromethylsulphonimide, which seems particularly difficult to prepare from trifluoromethanesulphonyl chloride. This is why one of the aims of the present invention is to provide a process which makes it possible to obtain fluorinated imides of the above type by using heavy sulphonyl halides (that is to say, halides corresponding to a halogen with an atomic number at least equal to that of chlorine).

It is preferable, for economic reasons, to use sulphonyl chlorides. This aim and others which will become apparent subsequently are achieved by means of a synthetic process which comprises a stage in which a nucleophile, the nucleophilic atom of which is a nitrogen, is brought into contact with a reactant comprising, for successive or simultaneous addition:

- a sulphonyl heavy halide (that is to say, in which the atomic number of the halogen is at least equal to that of chlorine), advantageously sulphonyl chloride; and
  - an organic base which simultaneously cannot be alkylated and is liposoluble;
- and with the condition that, when the nitrogen, the nucleophilic atom of the substrate, does not carry a sulphonyl functional group for which the carbon

part of the said sulphonyl heavy halide is perfluorinated on the carbon carried by the sulphur. However, in all cases, the process is particularly advantageous when the organic part of the said

sulphonyl heavy halide is chosen so that it is perfluorinated on the carbon carried by the sulphur.

Thus, the present invention provides a process for the synthesis of perfluorosulphonamides and of  
5 sulphonimides which exhibit at least one, advantageously two, sulphonyl group(s) for which the carbon adjoining the sulphur is perfluorinated.

The salts of these imides are prepared from these imides in a way known per se. The process  
10 according to the present invention can comprise a stage of preparation of these salts (as in the examples).

The notion of organic base which simultaneously cannot be alkylated and is liposoluble is explained subsequently.

15 The said nitrogen of the nucleophilic functional group advantageously carries a hydrogen or a negative charge (anion).

It is preferable for the said nitrogen of the nucleophilic functional group to carry two hydrogens  
20 (and even 3 in the specific case of ammonia or aqueous ammonia, which makes it possible to synthesize the preferred category of substrates, namely sulphamides, advantageously perfluorinated on the carbon adjoining the sulphur, preferably corresponding to the definition  
25 of Rf) or else to carry one hydrogen and one negative charge (anion).

In particular, the nucleophile can be a sulphonamide (sulphamide), in particular in the form of a salt, advantageously of an organic base which cannot  
30 be alkylated. The process is suitable in particular even when the organic part of the said sulphonamide (sulphamide) is perfluorinated on the carbon carried by the sulphur.

Conventional sulphamides (corresponding to non-  
35 perfluorinated sulphonic acids, such as  $\text{Ar-SO}_3\text{H}$ , with Ar representing an aryl, and  $\text{RSO}_3\text{H}$ , with R representing an alkyl) do not warrant being in the salt form, a salt

which would furthermore be difficult to obtain with the preferred bases of the invention.

The nucleophilic substrate thus exhibits, as nucleophilic functional group, a functional group  
5 advantageously chosen from sulphonamides of sulphonic acids in which the sulphur is bonded to an aryl or an aliphatic residue, including alkyls, preferably to an aliphatic residue perfluorinated on the carbon adjoining the sulphur. In general, the carbon number of  
10 the nucleophilic substrate varies from 1 to 15 and even from 1 to 10.

Thus, from the above and from the study which has led to the present invention, it is evident that the nucleophiles (in the neutral form or especially in  
15 the anion form) for which the problems, because they are difficult, are particularly well solved by the present invention are those for which the associated acid exhibits a  $pK_a$  at most equal to approximately 7, advantageously to 6, preferably to 5.

20 Ammonia constitutes a case apart and can, in the case of ammonia, result in an imide by two successive in situ condensations.

The condensation of the sulphonyl heavy halides targeted by the present invention with ammonia or  
25 aqueous ammonia can constitute a stage prior to the condensation of the amides.

In the present description, the term "approximately" is employed to underline the fact that the values which follow it have been rounded off  
30 mathematically and in particular that when the figure or figures furthest to the right of a number are zeros, these zeros are positional zeros and not significant

The said organic base which cannot be alkylated  
35 is advantageously chosen from hindered dialkylphosphines, trialkylphosphines, phosphonium hydroxides, hindered dialkylamines, trialkylamines or ammonium hydroxides. It is also possible to envisage phosphorus-

comprising and nitrogen-comprising rings exhibiting an appropriate basicity (see *infra*), for example nuclei of the pyridine type, but, according to the present invention and in contrast to standard techniques, these basic functional groups of aromatic heterocycles do not constitute the preferred bases.

It is desirable for the said base which simultaneously cannot be alkylated and is liposoluble to be chosen from hindered dialkylphosphines, trialkylphosphines, phosphonium hydroxides, hindered dialkylamines, trialkylamines or ammonium hydroxides.

It is recommended that the said base which simultaneously cannot be alkylated and is liposoluble should exhibit at least a significant (symbol "s" in the Handbook of Chemistry and Physics) solubility in benzene, advantageously a high (symbol "v" in the Handbook of Chemistry and Physics) solubility in benzene.

It is recommended that the substrate should exhibit at least a significant (symbol "s" in the Handbook of Chemistry and Physics) solubility in benzene, advantageously a high (symbol "v" in the Handbook of Chemistry and Physics) solubility in benzene.

Likewise, according to the present invention, it is preferable to see to it that the nucleophilic substrate is in the form of a salt of an organic base which cannot be alkylated, this optional saline compound between the organic base and the said substrate (when it is acidic, as in the case of perfluorosulphonamide) exhibiting at least a significant (symbol "s" in the Handbook of Chemistry and Physics) solubility in benzene, advantageously a high (symbol "v" in the Handbook of Chemistry and Physics) solubility in benzene.

In the preceding cases, it is, of course, particularly satisfactory for the solubility to be such that the benzene and the bases targeted above are

miscible in all proportions (symbol "∞" in the Handbook of Chemistry and Physics).

5 In choosing the base, it is advisable to observe basicity restrictions; thus, it is desirable for the  $pK_a$  of the acid associated with the said organic base (forming the optional salt with the nucleophile) to be greater than or in the region of that of the said nucleophile [for example sulphonamide (which in principle carries two hydrogens on the nitrogen)].

10 Likewise, it is also desirable for the  $pK_a$  of the acid associated with the said base which cannot be alkylated and is liposoluble to be equal to and preferably greater than that of the said sulphonamide.

15 When they are not the same, it is desirable for the difference between the  $pK_a$  values of the associated acids and that of the said nucleophile to be at least equal to 1, advantageously to 2, preferably to 3.

20 Although this is not preferred, the bases can be mixtures of bases, provided that the mixture meets the restrictions and, even preference, specified hereinabove.

25 It can be specified that, when the said nucleophile is sulphamide, for reasons of ease of handling, it is preferable for the said organic base which cannot be alkylated and the said base which simultaneously cannot be alkylated and is liposoluble to be identical. The reaction can be carried out without solvent, in particular when the organic bases are chosen from the preferred ones, that is to say particularly liposoluble and not very polar bases (for example and in particular, trialkylamines with a carbon

35 secondary or tertiary radical, advantageously two, or hindered dialkylamine).

As regards an advantageous implementation of the said stage, the operation of bringing into contact



is carried out in an organic solvent, advantageously of low polarity, preferably of low miscibility with water (at most 10% by mass, advantageously at most 5% by mass, preferably at most 2% by mass).

5       The reaction temperature is advantageously at least equal to the finishing melting point (apart from insolubles and in particular salts [hydrohalide, and the like]) of the reaction mixture and advantageously at most 100°C (advantageously two significant figures, preferably 3), advantageously to a temperature at most  
10       equal to approximately 50°C, preferably to 40°C and advantageously at least equal to 0. Thus, the reaction temperature is advantageously situated within the closed range defined by the finishing melting point and  
15       100°C, preferably within the range 0°C and 50°C, more preferably within the range 0 and 40°C. Although the reaction can be carried out under a different pressure, it is easier to carry it out at atmospheric pressure. In this case, it may be opportune to choose solvents so  
20       that there is a possible reflux at a temperature chosen within the above temperature ranges.

      In order to obtain good kinetics of reaction, it is recommended to carry out the said operation of bringing into contact in an organic solvent which is  
25       chosen so that, when the said nucleophile is sulphamide salt, the said salt is soluble therein, advantageously to a concentration level of at least 0.05M, preferably of at least 0.2M.

      To obtain the above solubilities, it is also  
30       possible to vary the said organic base which cannot be alkylated. It is also possible to vary the solvent and the organic base simultaneously.

      The bases employed in the present invention advantageously exhibit from 3 to approximately  
35       40 carbon atoms, preferably from 6 to approximately 30 carbon atoms, more preferably from 8 to 25 carbon atoms. In particular, when the carbon number is low (that is to say less than 7), it is preferable for at

least one of the substituents of the basic atom to be at least secondary. These bases are, for economic reasons, advantageously amines.

5 The bases can also be polyfunctional bases (for example, substituted ethylenediamines and in particular tetramethylethylenediamine), in which case the above restriction must be reduced to the number of useful basic functional groups.

10 The most useful solvents are solvents of relatively low polarity, of the chlorine solvent or aromatic solvent type, provided that, preferably, the said optional salt is sufficiently soluble therein.

15 The said solvent of low polarity, which, it should be remembered, can be a mixture, is advantageously chosen from those for which the polarity ( $E^f$ , expressed in kcal per mol) is at most equal to 40 (advantageously two significant figures).

20 However, for reasons of industrial hygiene and of environmental protection [some are already banned], non-aromatic chlorinated derivatives, in particular aliphatic chlorinated derivatives (such as methylene chloride or chloroform) or alkenic chlorinated derivatives (for example trichloroethylene), are generally to be avoided as solvent. Furthermore, although giving  
25 good results, they do not constitute the family with the best performance (thus, the solubility in water of methylene chloride is of the order of 2% by volume, i.e. 2.6% by mass).

30 Taking into account the above, the said solvent of low polarity is advantageously chosen from oxygen-comprising organic compounds (in particular ethers, esters, even ketones), hydrocarbons (including petroleum fractions) or ring-halogenated aromatic

35 Preferably, the said solvent of low polarity can advantageously be chosen from substituted benzenes and ring-halogenated aromatic hydrocarbons.

Respecting the stoichiometry of the reaction is desirable as regards the sulphonyl halide and the sulphonamide (sulphamide). A tolerance of plus or minus 20% is entirely acceptable and depends essentially on the respective cost of the reactants.

As regards the amount of the said base which cannot be alkylated and is liposoluble introduced during the reaction, it is at least equal to the amount necessary to neutralize the hydrohalic acid given off.

When the nitrogen of the substrate carries two hydrogens (three in the very particular case of ammonia, which makes it possible to synthesize, in particular in situ, the preferred category of substrates, namely sulphamides, advantageously perfluorinated on the carbon adjoining the sulphur, preferably corresponding to the definition of Rf; of course, in the case of an in situ synthesis, it is necessary to take into account the sulphonylation reaction of ammonia) and when the nucleophile is not in the salt form, it can be advantageous to bring the amount of base(s) introduced during the reaction to a value at least equal to twice the amount necessary to neutralize the hydrohalic acid given off.

In other words and more specifically, it is preferable for the sum of the bases (base of the substrate salt [see supra] and liposoluble organic base which cannot be alkylated) to be at least equal to the sum of the acidity given off in the form of hydrohalic acid and of the acidity of the sulphone compounds (in particular sulphonimides) being formed.

Thus, taking into account the above, it is desirable for the total amount of base(s) to be at least equal to one times the amount stoichiometrically necessary to neutralize the hydrohalic acid given off, advantageously at least equal to the sum of the acidity given off in the form of hydrohalic acid and of the acidity of the sulphone compounds (in particular sulphonimides); more specifically, it is recommended to

use an amount of base (expressed, of course, as equivalent) at least equal to the sum of the acidity of the sulphone compounds and of one and a quarter times the amount stoichiometrically necessary to neutralize the hydrohalic acid given off, advantageously at least equal to the sum of one and a half times the acidity given off in the form of hydrohalic acid and of the acidity of the sulphone compounds.

It is also preferable to avoid an excessively large excess of base(s); this is why it is desirable for the sum of the bases (base of the substrate salt [see supra] and liposoluble organic base which cannot be alkylated) to exhibit an excess, with respect to the sum of the acidity given off in the form of hydrohalic acid and of the acidity of the sulphone compounds being formed, at most equal to 3 times, advantageously to two times, preferably to one times the amount of hydrohalic acid given off.

The process with respect to the present invention is particularly advantageous for the synthesis of compounds obtained from sulphonyl chloride in which the organic part is perfluorinated (that is to say, corresponds to  $CX_2$ , see infra) on the carbon carried by the sulphur.

The present invention is targeted in particular at the case where the organic part of the said sulphonyl chloride is the same as that of the said sulphonamide.

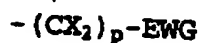
The present invention is also targeted at the case where the organic part of the said sulphonyl chloride carries, at least transiently in the form of a reaction intermediate, the sulphonamide functional group, which

person skilled in the art for condensation reactions, cyclization or polycondensation takes place according to the number of chain members separating the two functional groups and according to the dilution of the

reaction mixture (this well known phenomenon is recalled, inter alia, in the inserted application WO 97/23448).

The present invention is particularly useful for carrying out the condensation of the present invention when the organic parts, which are alike or different, of the said sulphonyl chloride and of the said sulphonamide are chosen from radicals of formula (Rf):

10



where:

- the X groups, which are alike or different, represent a fluorine or a radical of formula  $C_nF_{2n-1}$ , with n an integer at most equal to 5, preferably to 2;
- 15 • p represents an integer at most equal to 2;
- EWG represents an electron-withdrawing group, the possible functional groups of which are inert under the reaction conditions, advantageously fluorine or a perfluorinated residue of formula  $C_nF_{2n-1}$ , with n an integer at most equal to 8, advantageously to 5.

20

The total carbon number of Rf is advantageously between 1 and 15, preferably between 1 and 10.

EWG can be or carry a sulphonyl heavy halide functional group, which makes it possible to prepare, in situ, compounds carrying both the nucleophilic functional group and the sulphonyl heavy halide functional group, compounds where the organic part of the said sulphonyl chloride carries the sulphonamide functional group, which makes it possible to prepare cyclic products or polymeric products.

30

As was indicated above, the most advantageous compounds obtained from the imides synthesized according to the present invention are lithium derivatives, the said process advantageously comprising, after an optional purification and/or isolation stage, a stage of treatment with lithium hydroxide or a basic lithium salt.

35

According to the present invention, the starting sulphonamides can advantageously be synthesized by the action of the same sulphonyl halide as that used for the synthesis of the imide. This synthesis can be  
5 carried out in protic or aprotic polar solvents, provided that they have no tendency to be alkylated. In particular, the reaction can be carried out in symmetrical or unsymmetrical, cyclic or non-cyclic ethers.

10 Another aim of the present invention is to provide a reactant which is useful in the processes of the above type.

This aim, and others which will become apparent subsequently, is achieved by means of a reactant which  
15 comprises, for successive or simultaneous addition:

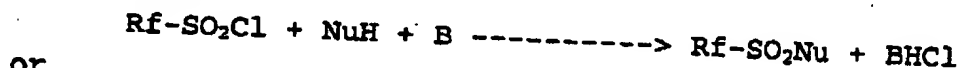
- a sulphonyl heavy halide (that is to say, in which the atomic number of the halogen is at least equal to that of chlorine), advantageously sulphonyl chloride, and;
  - 20 • an organic base which simultaneously cannot be alkylated and is liposoluble;
  - advantageously a solvent of low polarity;
- and by the fact that the organic part of the said sulphonyl is perfluorinated on the carbon carried by  
25 the sulphur.

Another aim of the present invention is to provide for the use of sulphonyl chloride, perfluorinated on the carbon carried by the sulphur, that is to say adjoining it, in the mono- and bissulphonyl-  
30 ation of ammonia, aqueous ammonia or amide, including sulphamide, advantageously in the presence of an organic base which cannot be alkylated and is lipo-

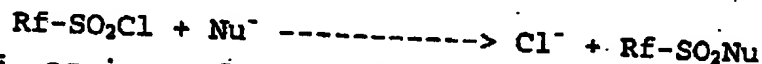
35 at least one, preferably two, sulphone groups perfluorinated on the aliphatic carbon (that is to say sp<sup>3</sup> carbon) adjoining the sulphur.

One of the advantages of the use of the chloride is a low sensitivity to side reactions with water.

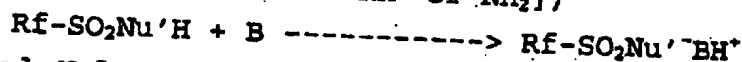
In order to better understand the invention, the following typical reactions can be given by way of indication:



or



and if, as is preferred, Nu is Nu'H in nature (or, more specifically, if the nucleophilic functional group under consideration of Nu has the structure -NH- [that is to say, the structure NH<sup>-</sup> or NH<sub>2</sub>])



NuH and Nu<sup>-</sup> respectively represent the nucleophile in the neutral and anionic form.

The most advantageous substrates are those where Nu is chosen from Ar-SO<sub>2</sub>-NH-, in particular R-SO<sub>2</sub>-NH-, including and preferably Rf-SO<sub>2</sub>-NH-.

The following non-limiting examples illustrate the invention:

**Example 1: Preparation of trifluoromethanesulphonamide:**  
**CF<sub>3</sub>SO<sub>2</sub>NH<sub>2</sub>**

25

- reaction in anhydrous medium:

15.3 g of trifluoromethanesulphonyl chloride, in solution in 103 g of anhydrous isopropyl ether, are charged to a reactor. The mixture is cooled to 5°C and ammonia is slowly added over 2 h. After stirring for 5 h at 5°C, 24.8 g of water are added in order to dissolve the salts. The mixture is subsequently acidified by addition of 20.7 g of a 36% aqueous hydrochloric acid solution.

35

After a further addition of 13 g of water, the phases are separated. The aqueous phase is washed with 50 g of isopropyl ether. The organic phases are com-

bined and the solvent is removed under reduced pressure.

10.15 g of trifluoromethanesulphonamide as a white solid are thus obtained.

5 Melting point (Koffler) = 119°C.

- reaction in aqueous medium:

The reaction is carried out analogously by using a 30% aqueous ammonia solution.

10 Example 2: Preparation of lithium bistrifluoromethylsulphonimide

1 l of monochlorobenzene and 164.6 g of trifluoromethanesulphonamide, prepared according to the preceding example, are charged to a reactor. 224.6 g of triethylamine are subsequently added to this suspension. The solution obtained is cooled to 5°C. A solution of 187 g of trifluoromethanesulphonyl chloride in 191 g of monochlorobenzene is subsequently added over 40 min at 0-5°C.

The temperature is subsequently brought to 28°C. After reacting for 4 h, the reaction mixture is filtered.

25 The filtrate is degassed by bubbling nitrogen and then washed with 436 g of water. The 2 lower organic phases are recovered and again washed with 507 g of water.

30 These organic phases are subsequently treated with a solution of 46.7 g of lithium hydroxide hydrate in 216 g of water. The mixture obtained contains two phases.

The aqueous phase is recovered and extracted with 226 g of isopropyl ether.

35 reduced pressure to result in 206 g of crude lithium bistrifluoromethanesulphonimide in the form of a yellowish solid.

Yd = 60%



$^{19}\text{F}$  NMR = -1.8 ppm

Example 3: Reaction in the presence of diisopropylethylamine

5

11.2 g (0.079 m) of the amide of trifluoromethanesulphonic acid in 73 g of monochlorobenzene are charged to a reactor. After addition of 20.7 g (0.16 m) of diisopropylethylamine, 14.7 g (0.087 m) of trifluoromethanesulphonyl chloride, in solution in 15 g of monochlorobenzene, are run in at 10°C for 45 min. The mixture is subsequently stirred for 4 h at 30°C.

10 The treatment is carried out as in the preceding example and results in 20.4 g of lithium bistrifluoromethanesulphonimide assaying at 98% (yd = [(20.4/303)/0.079] × 0.98 = 83%).

15

Examples 11 to 13: Role of the solvent

20

To give a better demonstration of the role of the solvent, use was made of a base, the salt of which exhibits mediocre solubility:

Example No.	Reactants	Solvent	Conditions	Results
4	CF <sub>3</sub> SO <sub>2</sub> NH <sub>2</sub> = 1.6 g CF <sub>3</sub> SO <sub>2</sub> Cl = 1 eq. NEt <sub>3</sub> = 2 eq.	CH <sub>2</sub> Cl <sub>2</sub>	Addition CF <sub>3</sub> SO <sub>2</sub> Cl at 0°C Reaction 13 h at 20°C	Conversion CF <sub>3</sub> SO <sub>2</sub> NH <sub>2</sub> =80% Yield = 43%
5	CF <sub>3</sub> SO <sub>2</sub> NH <sub>2</sub> = 3.1 g CF <sub>3</sub> SO <sub>2</sub> Cl = 1 eq. NEt <sub>3</sub> = 2 eq.	CH <sub>2</sub> Cl <sub>2</sub>	Introduction CH <sub>2</sub> Cl <sub>2</sub> +CF <sub>3</sub> SO <sub>2</sub> NH <sub>2</sub> + 1 eq. NEt <sub>3</sub> Addition CF <sub>3</sub> SO <sub>2</sub> Cl at 0°C Run in 1 eq. NEt <sub>3</sub> at 0°C Reaction 3 h at 20°C	Conversion CF <sub>3</sub> SO <sub>2</sub> NH <sub>2</sub> =76% Yield = 31%
6	CF <sub>3</sub> SO <sub>2</sub> NH <sub>2</sub> = 1.4 g CF <sub>3</sub> SO <sub>2</sub> Cl = 1 eq. NEt <sub>3</sub> = 2 eq.	DIPE	Addition CF <sub>3</sub> SO <sub>2</sub> Cl at 0°C Reaction 3 h at 20°C	Conversion CF <sub>3</sub> SO <sub>2</sub> NH <sub>2</sub> =80% Yield = 33%
7	CF <sub>3</sub> SO <sub>2</sub> NH <sub>2</sub> = 1 g CF <sub>3</sub> SO <sub>2</sub> Cl = 1 eq. NEt <sub>3</sub> = 2 eq.	MCB	Addition CF <sub>3</sub> SO <sub>2</sub> Cl at 0°C Reaction 13 h at 20°C	Quantitatively determined yield = 67%
8	CF <sub>3</sub> SO <sub>2</sub> NH <sub>2</sub> = 1.85 g CF <sub>3</sub> SO <sub>2</sub> Cl = 1 eq. Pyridine = 2 eq.	CH <sub>2</sub> Cl <sub>2</sub>	Addition CF <sub>3</sub> SO <sub>2</sub> Cl at 0°C Reaction 7 h at 30°C Autogenous pressure	Conversion CF <sub>3</sub> SO <sub>2</sub> NH <sub>2</sub> =35% Yield = 24%
9	CF <sub>3</sub> SO <sub>2</sub> NH <sub>2</sub> = 1.62 g CF <sub>3</sub> SO <sub>2</sub> Cl = 1.1	DIPE	Addition CF <sub>3</sub> SO <sub>2</sub> Cl at 0°C	Conversion CF <sub>3</sub> SO <sub>2</sub> NH <sub>2</sub> =30%
	Pyridine = 2 eq.		Autogenous pressure	

Example No.	Reactants	Solvent	Conditions	Results
10	$\text{CF}_3\text{SO}_2\text{NH}_2 = 1.02 \text{ g}$ $\text{CF}_3\text{SO}_2\text{Cl} = 1.1 \text{ eq.}$ Pyridine = 2 eq.	MCB	Addition $\text{CF}_3\text{SO}_2\text{Cl}$ at $0^\circ\text{C}$ Reaction 7 h at $30^\circ\text{C}$ Autogenous pressure	Conversion $\text{CF}_3\text{SO}_2\text{NH}_2 = 63\%$ Yield = 4%
11	$\text{CF}_3\text{SO}_2\text{NH}_2 = 1.91 \text{ g}$ $\text{CF}_3\text{SO}_2\text{Cl} = 1.1 \text{ eq.}$ DIPEA = 2 eq.	$\text{CH}_2\text{Cl}_2$	Addition $\text{CF}_3\text{SO}_2\text{Cl}$ at $0^\circ\text{C}$ Reaction 7 h at $20^\circ\text{C}$	Conversion $\text{CF}_3\text{SO}_2\text{NH}_2 = 92\%$ Yield = 85%
12	$\text{CF}_3\text{SO}_2\text{NH}_2 = 1.28 \text{ g}$ $\text{CF}_3\text{SO}_2\text{Cl} = 1.2 \text{ eq.}$ DIPEA = 2 eq.	DIPEA	Addition $\text{CF}_3\text{SO}_2\text{Cl}$ at $0^\circ\text{C}$ Reaction 8 h at $20^\circ\text{C}$	Conversion $\text{CF}_3\text{SO}_2\text{NH}_2 > 91\%$ Yield = 90%
13	$\text{CF}_3\text{SO}_2\text{NH}_2 = 1.2 \text{ g}$ $\text{CF}_3\text{SO}_2\text{Cl} = 1.2 \text{ eq.}$ DIPEA = 2 eq.	MCB	Addition $\text{CF}_3\text{SO}_2\text{Cl}$ at $0^\circ\text{C}$ Reaction 8 h at $20^\circ\text{C}$	Conversion $\text{CF}_3\text{SO}_2\text{NH}_2 > 98\%$ Yield = 97%

DIPE: diisopropyl ether  
MCB: monochlorobenzene  
DIPEA: diisopropylethylamine

5

\* The analyses of the various tests were carried out by fluorine NMR spectroscopy with internal standard.

CLAIMS

1. (Perfluoro)sulphonylation process, characterized in that it comprises a stage in which a nucleophile, the nucleophilic atom of which is a nitrogen, is brought into contact with a reactant comprising, for successive or simultaneous addition:
  - a sulphonyl heavy halide, advantageously sulphonyl chloride, and;
  - an organic base which simultaneously cannot be alkylated and is liposoluble;and with the condition that, when the nitrogen, the nucleophilic atom of the substrate, does not already carry a sulphonyl functional group for which the carbon adjoining the sulphur is perfluorinated, the organic part of the said sulphonyl heavy halide is perfluorinated on the carbon carried by the sulphur.
2. Process according to claim 1, characterized in that the said nucleophile, in the neutral or anionic form, has, as associated acid, an acid for which the  $pK_a$  is at most equal to approximately 7, advantageously to 6, preferably to 5.
3. Process according to claims 1 and 2, characterized in that the said nitrogen of the said nucleophile is connected to an electron-withdrawing group, advantageously a sulphonyl group; advantageously the said nucleophile is chosen from sulphamides of sulphonic acids in which the sulphur is bonded to an aryl or from sulphamides of sulphonic acids in which the sulphur is bonded to an aliphatic residue, including alkyls, preferably from sulphamides of sulphonic acids in which the sulphur is bonded to an aliphatic residue perfluorinated on the carbon
4. Process according to claims 1 to 3, characterized in that the said nucleophile is a salt of sulphonamide (sulphamide) and of an organic base which cannot be alkylated.

5. Process according to claims 1 to 4, characterized in that the said nucleophile is a sulphonamide (sulphamide) in the form of a liposoluble salt with the said organic base which simultaneously cannot be alkylated and is liposoluble.

6. Process according to claims 1 to 5, characterized in that the said organic base which cannot be alkylated is chosen from hindered dialkylphosphines, trialkylphosphines, phosphonium hydroxides, hindered dialkylamines, trialkylamines or ammonium hydroxides.

7. Process according to claims 1 to 6, characterized in that the said base which simultaneously cannot be alkylated and is liposoluble is chosen from hindered dialkylphosphines, trialkylphosphines, phosphonium hydroxides, hindered dialkylamines, trialkylamines or ammonium hydroxides.

8. Process according to claims 1 to 7, characterized in that the said base which simultaneously cannot be alkylated and is liposoluble exhibits at least a significant (symbol "s" in the Handbook of Chemistry and Physics) solubility in benzene, advantageously a high (symbol "v" in the Handbook of Chemistry and Physics) solubility in benzene.

9. Process according to claims 1 to 8, characterized in that the said organic base exhibits at least a significant (symbol "s" in the Handbook of Chemistry and Physics) solubility in benzene, advantageously a high (symbol "v" in the Handbook of Chemistry and Physics) solubility in benzene.

10. Process according to claims 1 to 9, characterized in that the  $pK_a$  of the acid associated with the said organic base is greater than or equal to that of the said sulphonamide.

11. Process according to claims 1 to 10, characterized in that the  $pK_a$  of the acid associated with the said base which cannot be alkylated and is

liposoluble is greater than or equal to that of the said sulphonamide.

12. Process according to claims 1 to 11, characterized in that, when the said nucleophile is a salt of sulphonamide (sulphamide) and of an organic base which cannot be alkylated, the said organic base which cannot be alkylated and the said base which simultaneously cannot be alkylated and is liposoluble are identical.

13. Process according to claims 1 to 12, characterized in that the said operation of bringing into contact is carried out in an organic solvent, advantageously of low polarity, preferably of low miscibility with water (at most 10% by mass, advantageously at most 5% by mass, preferably at most 2% by mass).

14. Process according to claims 1 to 13, characterized in that, the said operation of bringing into contact is carried out in an organic solvent which is chosen so that the said salt is soluble therein, advantageously to a concentration level of at least 0.05M, preferably of at least 0.2M.

15. Process according to claims 1 to 14, characterized in that the amount of the said base which cannot be alkylated and is liposoluble introduced during the reaction is at least equal to the amount necessary to neutralize the hydrohalic acid given off.

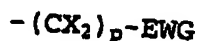
16. Process according to claims 1 to 15, characterized in that the organic part of the said sulphonyl chloride is perfluorinated on the carbon carried by the sulphur.

17. Process according to claims 1 to 16,

35 sulphonyl chloride is the same as that of the said sulphonamide.

18. Process according to claims 1 to 17, characterized in that the organic parts, which are alike or different, of the said sulphonyl chloride and

of the said sulphonamide are chosen from radicals of formula (Rf):



5 where:

- the X groups, which are alike or different, represent a fluorine or a radical of formula  $C_nF_{2n+1}$ , with n an integer at most equal to 5, preferably to 2;
- p represents an integer at most equal to 2;
- 10 • EWG represents an electron-withdrawing group, the possible functional groups of which are inert under the reaction conditions, advantageously fluorine or a perfluorinated residue of formula  $C_nF_{2n+1}$ , with n an integer at most equal to 8, advantageously to 5.

15 The total carbon number of Rf is advantageously between 1 and 15, preferably between 1 and 10.

19. Process according to claims 1 to 18, characterized in that the said nucleophile in which the nucleophilic atom is a nitrogen is a salt of  
20 sulphonamide (sulphamide) and of an organic base which cannot be alkylated and in that the said process comprises, after an optional purification and/or isolation stage, a stage of treatment with lithium hydroxide or a basic lithium salt.

25 20. Reactant of use in the implementation of the process according to claims 1 to 19, characterized in that it comprises, for successive or simultaneous addition:

- a sulphonyl heavy halide (that is to say, in which  
30 the atomic number of the halogen is at least equal to that of chlorine), advantageously sulphonyl chloride, and;
  - an organic base which simultaneously cannot be alkylated and is liposoluble;
  - 35 • a solvent of low polarity;
- and in that the organic part of the said sulphonyl is perfluorinated on the carbon carried by the sulphur.

21. Reactant according to claim 20, characterized in that the said solvent, including mixture of solvents, of low polarity is chosen from those exhibiting a low solubility in water and not exhibiting a chlorinated aliphatic chain.
- 5 22. Reactant according to claims 20 and 21, characterized in that the said solvent of low polarity is chosen from those for which the polarity ( $E^f$ , expressed in kcal per mol) is at most equal to 40
- 10 (advantageously two significant figures).
23. Reactant according to claims 20 to 22, characterized in that the said solvent of low polarity is chosen from oxygen-containing organic compounds (in particular ethers, esters, even ketones), hydrocarbons
- 15 (including petroleum fractions) or ring-halogenated aromatic hydrocarbons.
24. Reactant according to claims 20 to 23, characterized in that the said solvent of low polarity is chosen from substituted benzenes and ring-
- 20 halogenated aromatic hydrocarbons.

DATED THIS 18TH DAY OF MAY 1998



JOHN & KERNICK  
FOR THE APPLICANT



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ACCESSION NUMBER: 1991-354967 [49] WPIX  
DOC. NO. NON-CPI: N1991-271636  
DOC. NO. CPI: C1991-153052  
TITLE: Charge transfer complexes of peri-xanthene-xanthene - used as antistatic agents  
in plastics and as organic conductors in electronics.

DERWENT CLASS: A60 E13 L03 X12 X25  
INVENTOR(S): HASSEL, T; HEYWANG, G

PATENT ASSIGNEE(S): (FARB) BAYER AG

COUNTRY COUNT: 1

PATENT INFORMATION:

PATENT NO	KIND	DATE	WEEK	LA	PG
DE---	4016535	A	19911128	(199149) *	<--

APPLICATION DETAILS:

PATENT NO	KIND	APPLICATION	DATE
DE---	4016535	A	1990DE-4016535 19900523 <--

PRIORITY APPLN. INFO: 1990DE-4016535 19900523

AB DE 4016535 A UPAB: 19930928

Charge transfer (CT) complexes (I) of peri-xantheneoxanthene of formula (I) are claimed: n = total of positively charged and neutral peri-xantheneoxanthene molecules (1-5); A- = monovalent complex anion. Also claimed is the mfr. of (I) by oxidn. of peri-xantheneoxanthene.

A(-) is pref. a hydrogensulphate-, methylsulphate-, dodecylsulphate-, methylsulphonate, dodecylsulphonate-, tosylate-, perchlorate-, tetrafluoroborate-, hexafluorophosphate-, hexafluoroarsenate-, hexafluoroantimonate-, tribromocuprate- and trichlorocuprate-anion and esp. a methylsulphonate, tosylate, perchlorate-, tetrafluoroborate-, hexafluorophosphate- or a tribromocuprate-anion.

USE/ADVANTAGE - (I) are used as antistatic agents in plastics and as organic conductors in electronics (claimed). The radical cation salts of peri-xantheneoxanthene are stable at temps. up to 300 deg. C and exhibit good electrical conductivity and are non-corrosive. (4pp Dwg.No.0/0)

